Royal Netherlands Institute for Sea Research

Passive sampling of nonpolar compounds in sediments

Kees Booij (NIOZ, NL)
Foppe Smedes (Deltares, NL)

SERDP/ESTCP Passive sampling session
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14. ABSTRACT
Passive sampling is a powerful tool for determining the concentrations of truly dissolved contaminants in pore waters as well as for measuring the size of the exchangeable contaminant fraction in the sediment phase. Application of passive sampling of nonpolar contaminants in sediments is technically easy, but conceptually difficult, compared with traditional batch water sampling. The sorption capacity of the samplers and the (equivalent) water sampling rate are the two parameters that are needed to conceptualize the sampling process. These parameters also determine the value of the detection limits and the rate at which passive samplers equilibrate with their environment. After discussing contaminant uptake by passive samplers in an infinite water volume, their behavior in sediments will be dealt with using two practical examples. Exposure to stagnant sediments will be contrasted with exposure to sediment slurries. Passive sampler exposure to sediment slurries at low sampler/sediment phase ratios allows concentrations of dissolved contaminants in the pore water to be estimated. Exposure at high sampler/sediment phase ratios yields information on the size of the contaminant fraction in the sediment that is easily exchangeable with the pore water. Guidelines for designing passive sampler exposures to contaminated sediments will be discussed, and sources of uncertainties in the results will be highlighted.

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PASSIVE SAMPLING OF NONPOLAR COMPOUNDS IN SEDIMENTS

KEES BOOIJ
Royal Netherlands Institute for Sea Research
P.O. Box 59
Texel, 1790 AB NETHERLANDS
+31 222 369 463
kees.booij@nioz.nl

CO-PERFORMER: Foppe Smedes (Deltares)

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Nonpolar samplers for analytes with logK_{ow} > 4

Technically simple

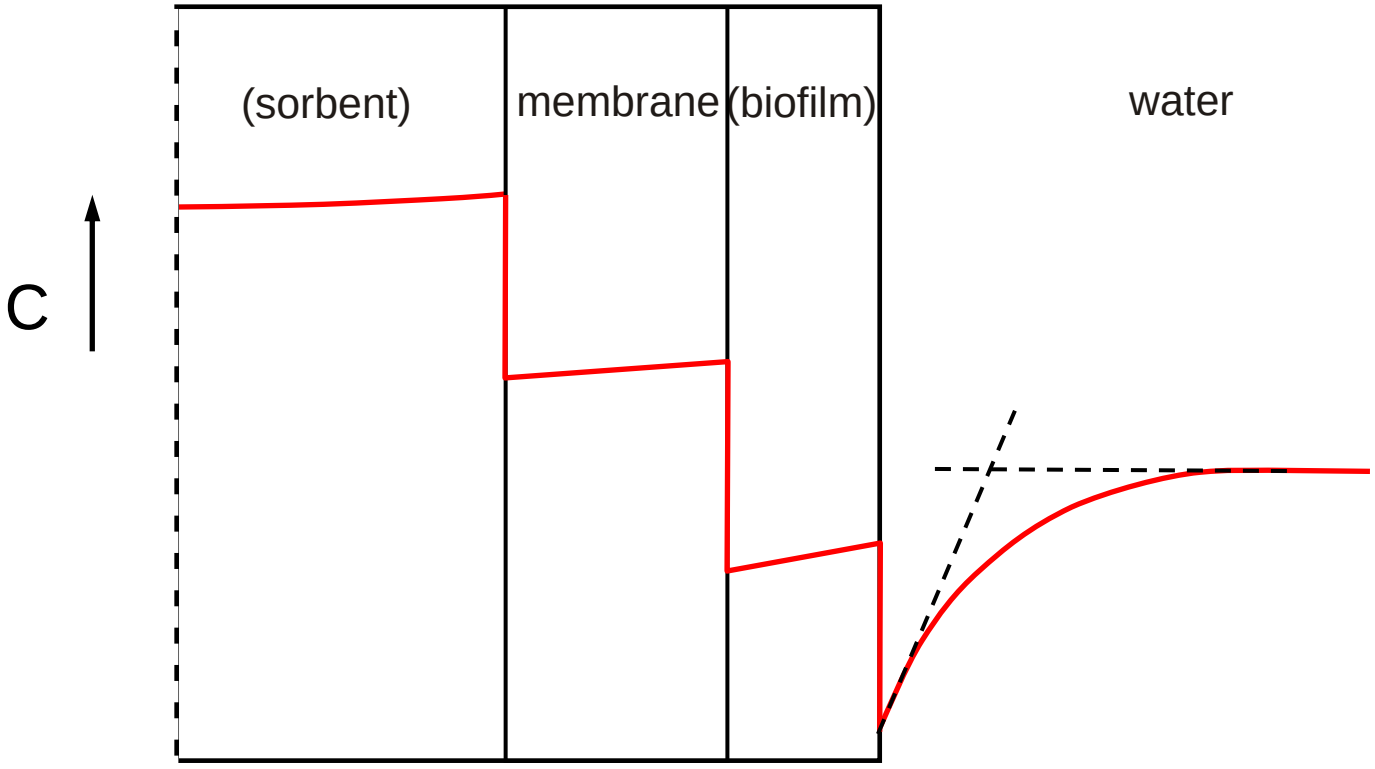
Conceptually difficult (initially)

Outline

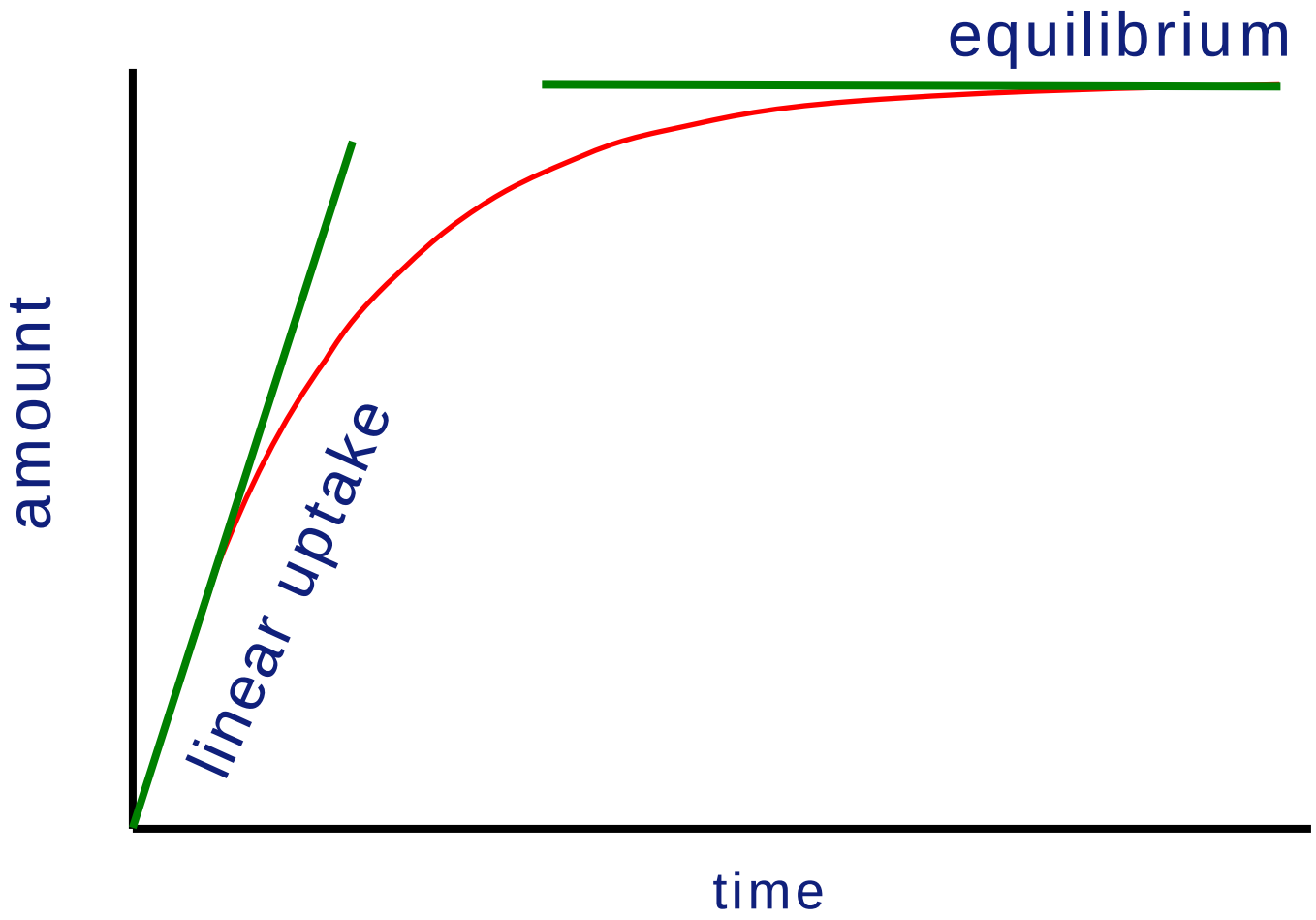
- **Theory**
  - working principles
  - concepts & link to batch sampling
    - sampling rates and sorption capacity
    - equilibration times and detection limits
  - sampling rate calibration
  - finite water volumes and sediment slurries
- **Practice**
  - pore water extraction (measuring C_w)
  - sediment extraction (measuring accessible fractions)
- **Achievements & caveats**

PSDs in water (infinite volume)

Workingprinciple

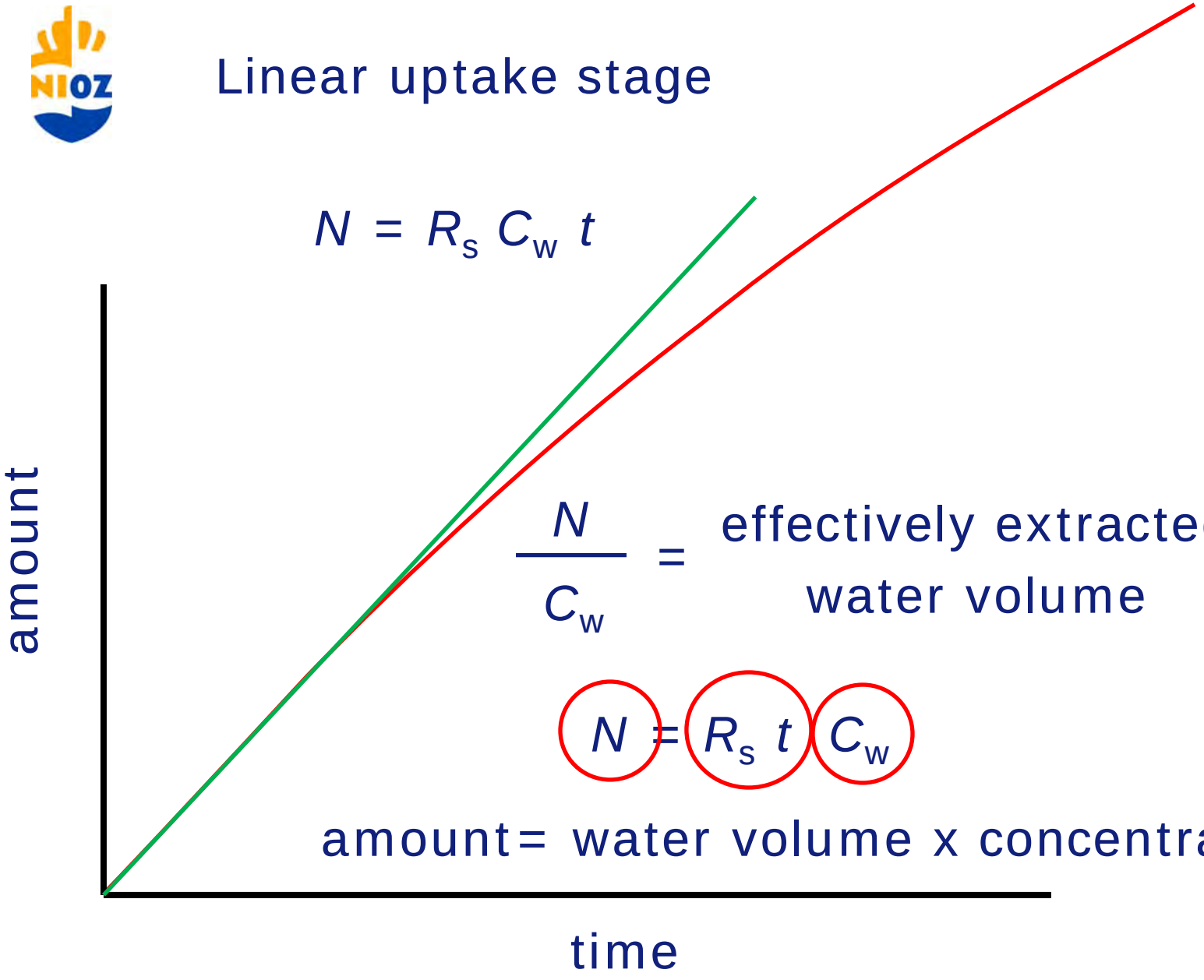


Uptake kinetics



Linear uptake stage

$$N = R_s C_w t$$



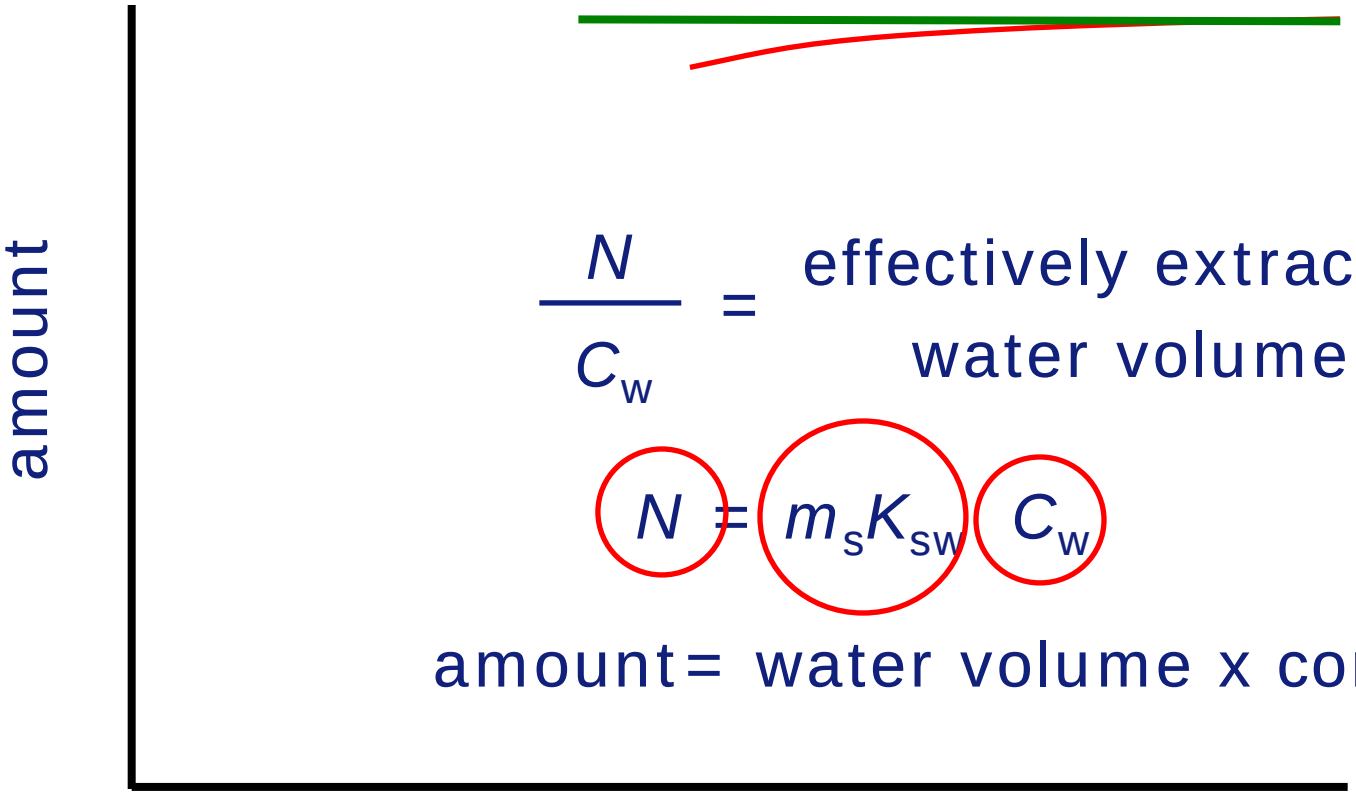
$$\frac{N}{C_w} = \text{effectively extracted water volume} = R_s t$$

$$N = R_s t C_w$$

amount = water volume x concentration

Equilibrium stage

$$\frac{N}{m_s} = K_{sw}\, C_w$$



$$\frac{N}{C_w} = \text{effectively extracted water volume} = m_s\, K_{sw}$$

$$N = m_s K_{sw}\, C_w$$

amount = water volume x concentration

Uptake model (infinite water volume)

$$N = C_w \; K_{sw}\, m_s \left[1 - \exp\left(-\frac{R_s\, t}{K_{sw}\, m_s}\right)\right]$$

Amount = concentration x water volume

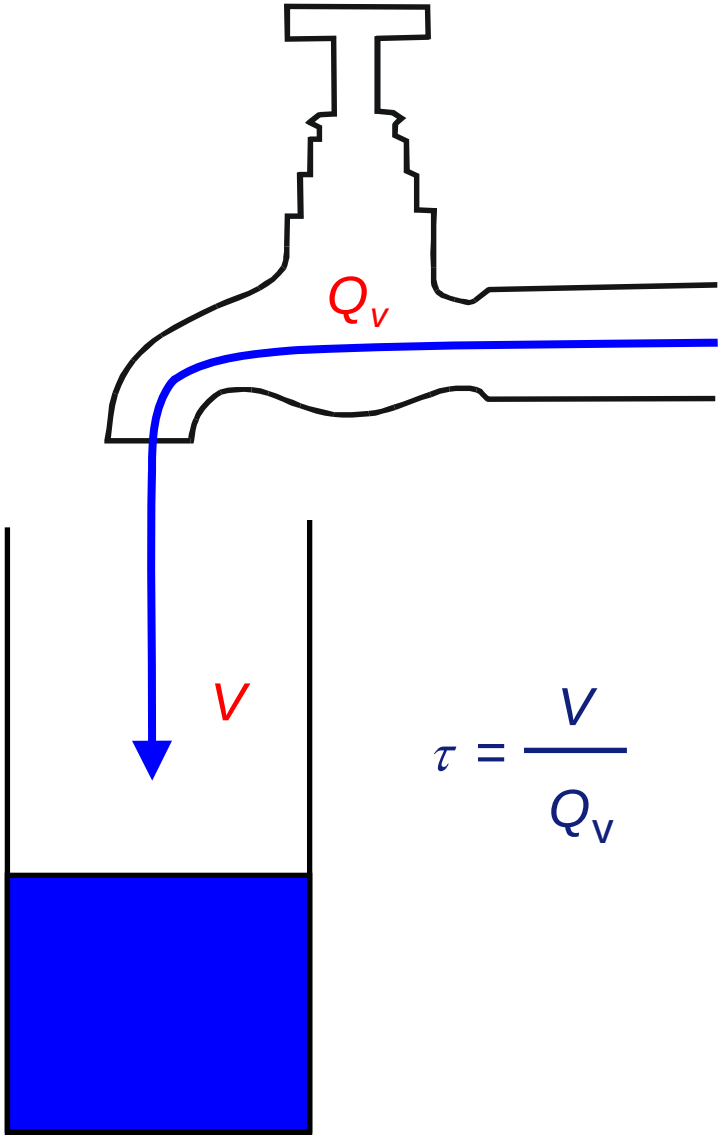
Equilibration time (TWA window)

$R_s\ C_w$

$K_{sw}\ m_s C_w$

$R_s\ \tau = K_{sw}\ m_s$

$\tau = \dfrac{K_{sw}\ m_s}{R_s}$



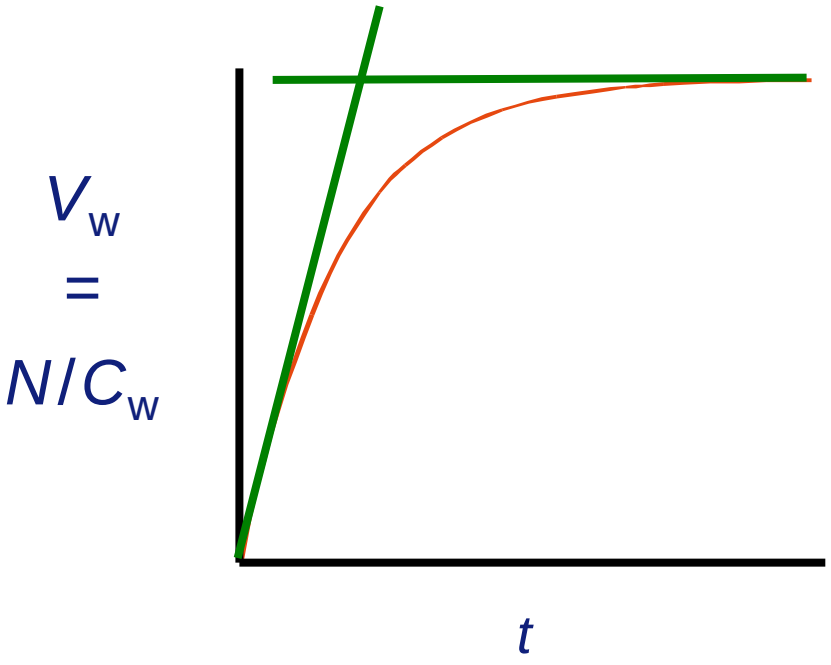
$\tau = \dfrac{V}{Q_v}$

Detection limits

Linear uptake stage $V_{wLUS} = R_s\, t$

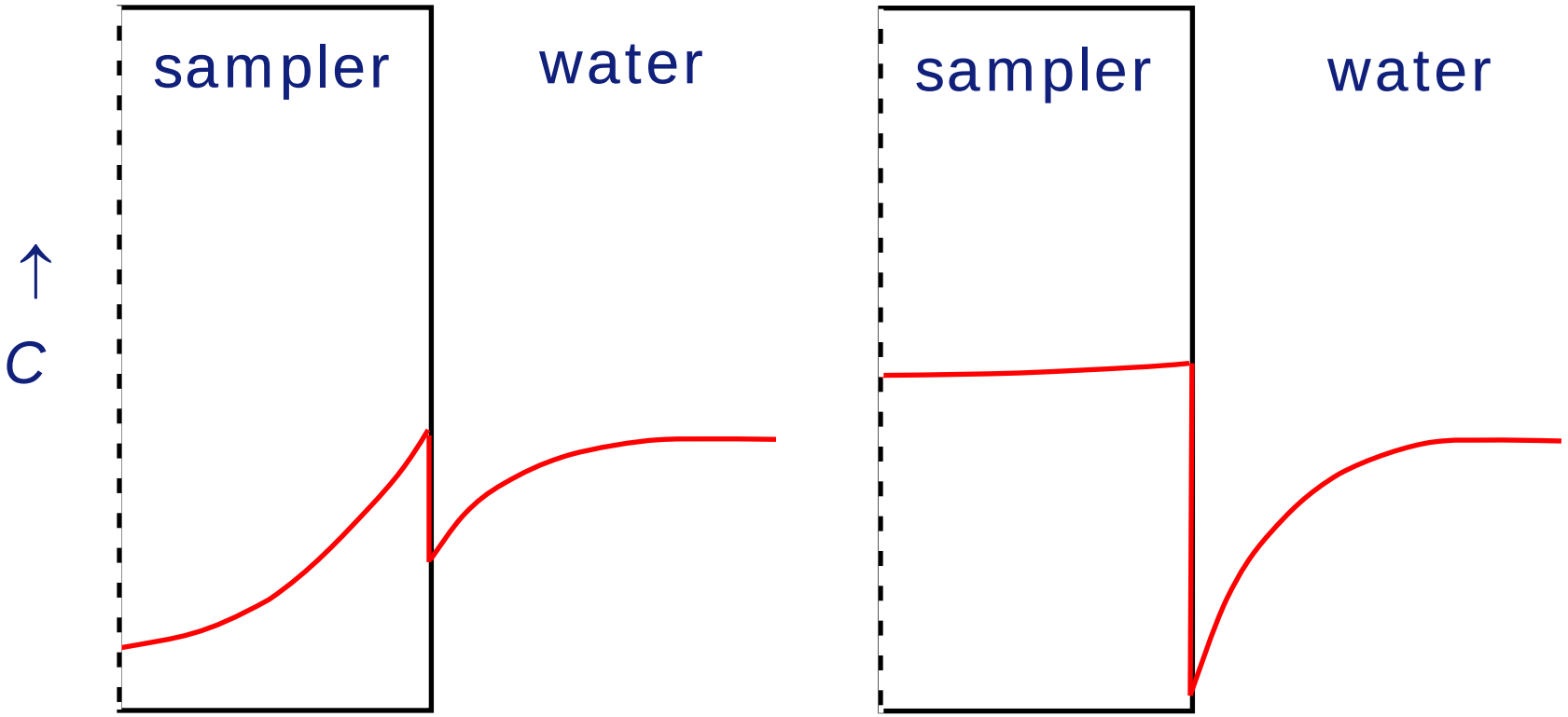
Equilibrium stage $V_{wEqS} = m_s\, K_{sw}$

take the lowest of these



$$DL_{Cw} = \frac{DL_N}{V_w}$$

Uptake rate control



membrane-control

$R_s \sim K_{sw} D_m$

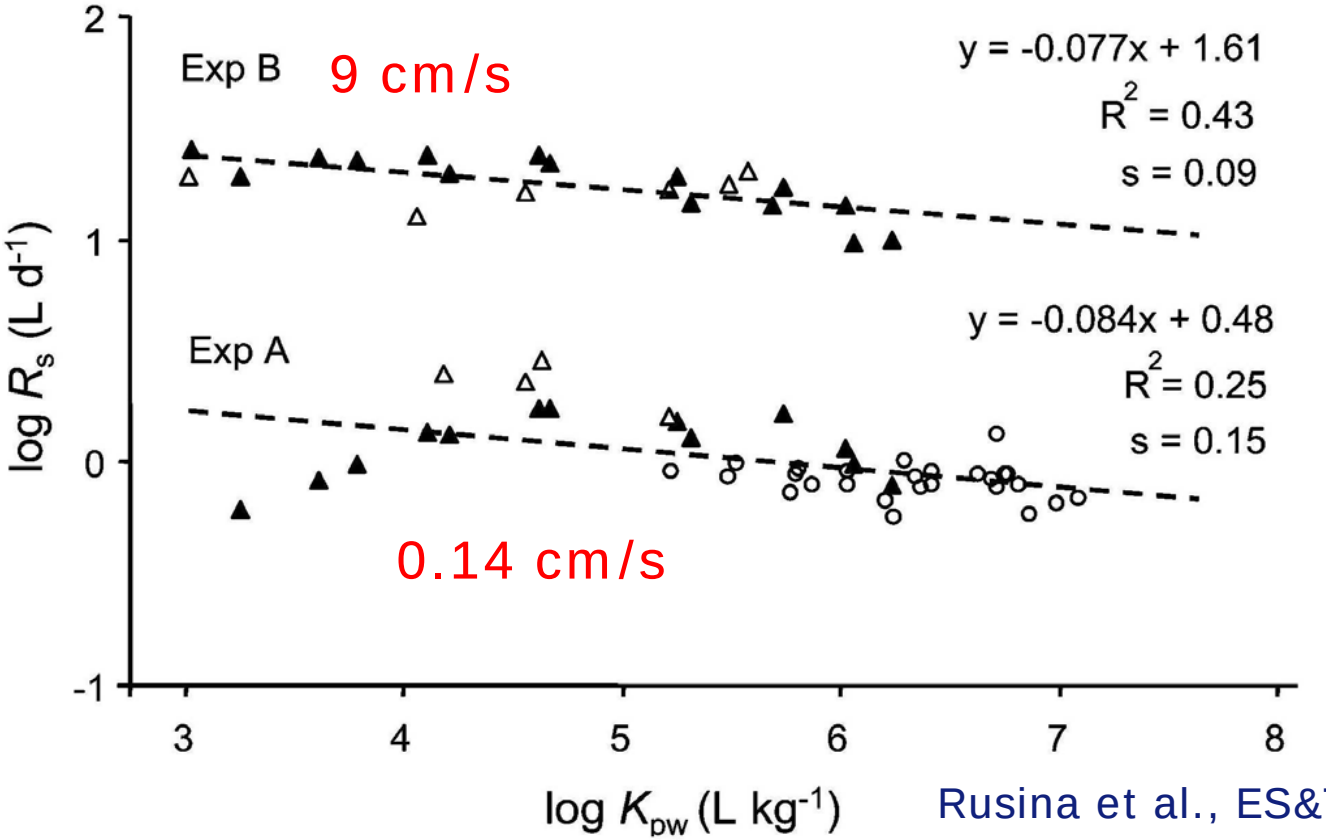
WBL-control

$R_s \sim D_w^{2/3}$

Sampling rates (R_s)

compound properties (diffusion coefficient, hydrophobicity)

- temperature
- flow rate
- suspended solids concentration



Rusina et al., ES&T 44:362–367, 2010

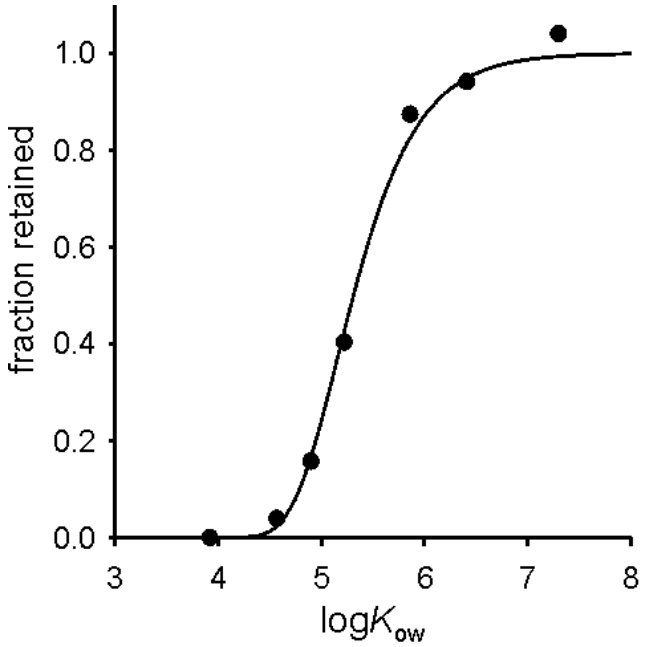
Calibration of uptake kinetics

Performance reference compounds

- not occurring in the water
- spiked into PSD before exposure
- dissipation follows: $\frac{N_s}{N_0} = \exp\left(-\frac{R_s\ t}{K_{sw}\ V_s}\right)$

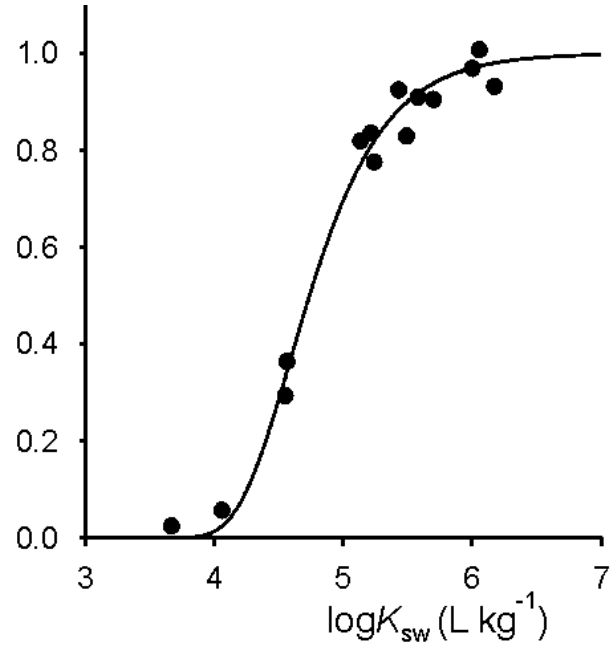
SPMD in water

$R_s = 5.1 \pm 0.3$ L d^{-1}



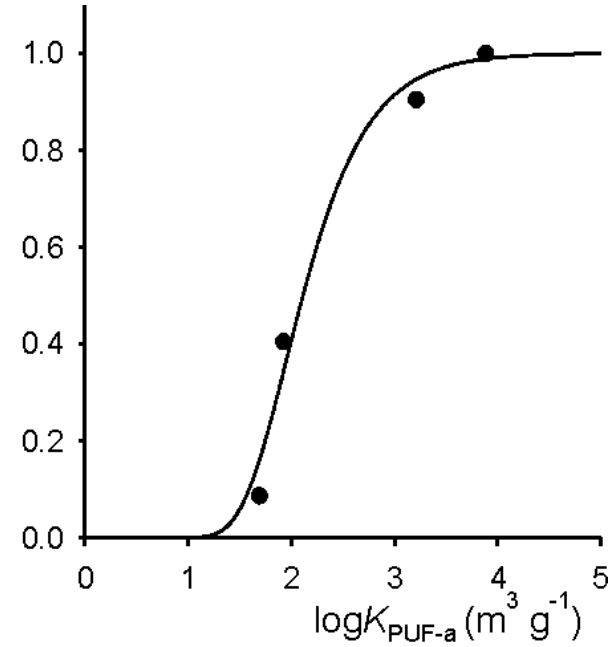
silicone in water

$R_s = 11.6 \pm 0.7$ L d^{-1}



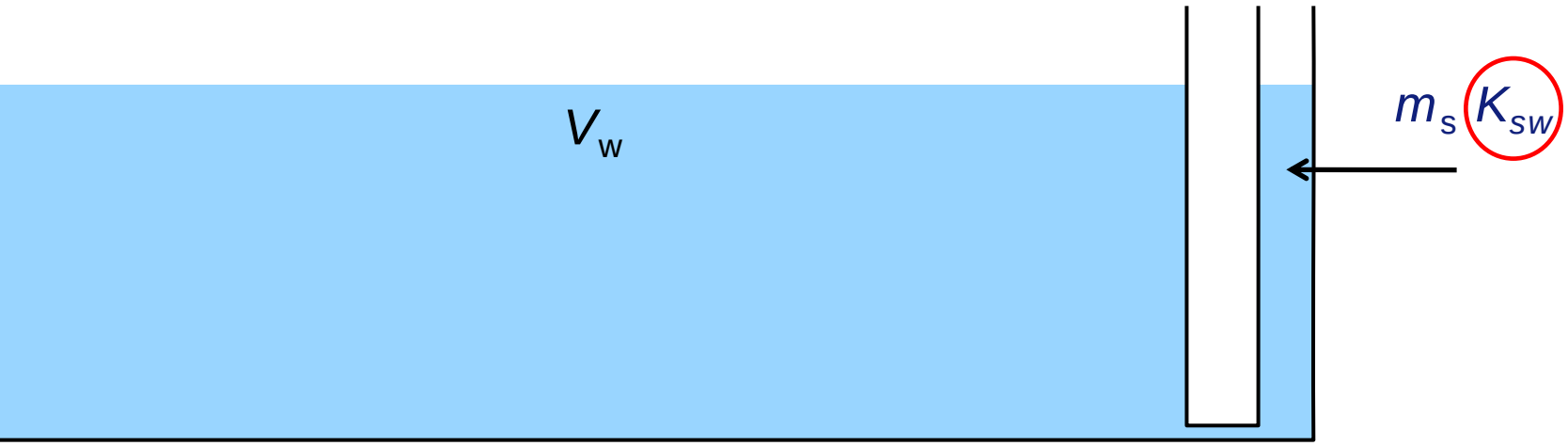
PUF in air

$R_s = 5.6 \pm 0.6$ m^3 d^{-1}



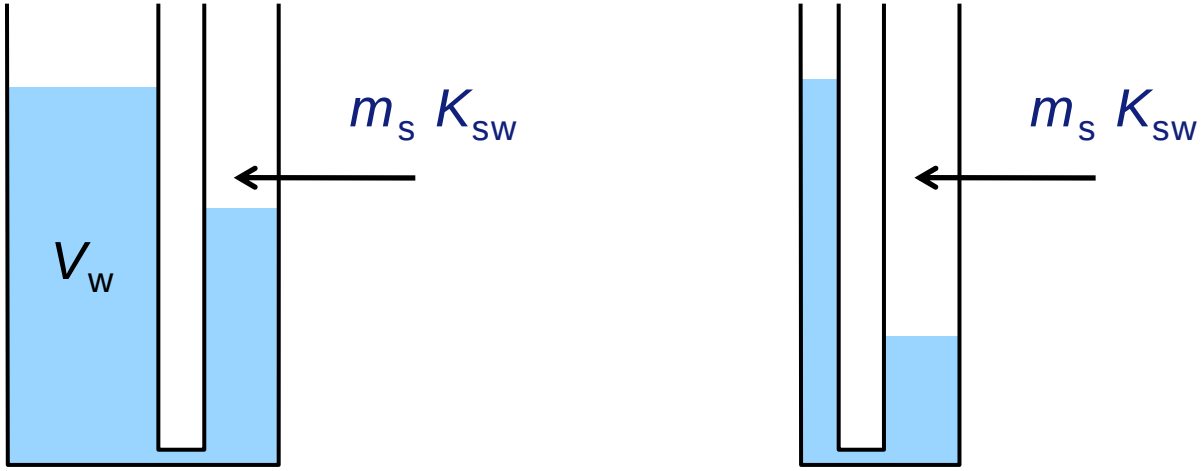
PSDs in water (finite volume)

Infinite water volume



"infinite" means: $V_w >> m_s K_{sw}$

Finite water volume



"finite" means: $V_w \cong m_s\ K_{sw}$

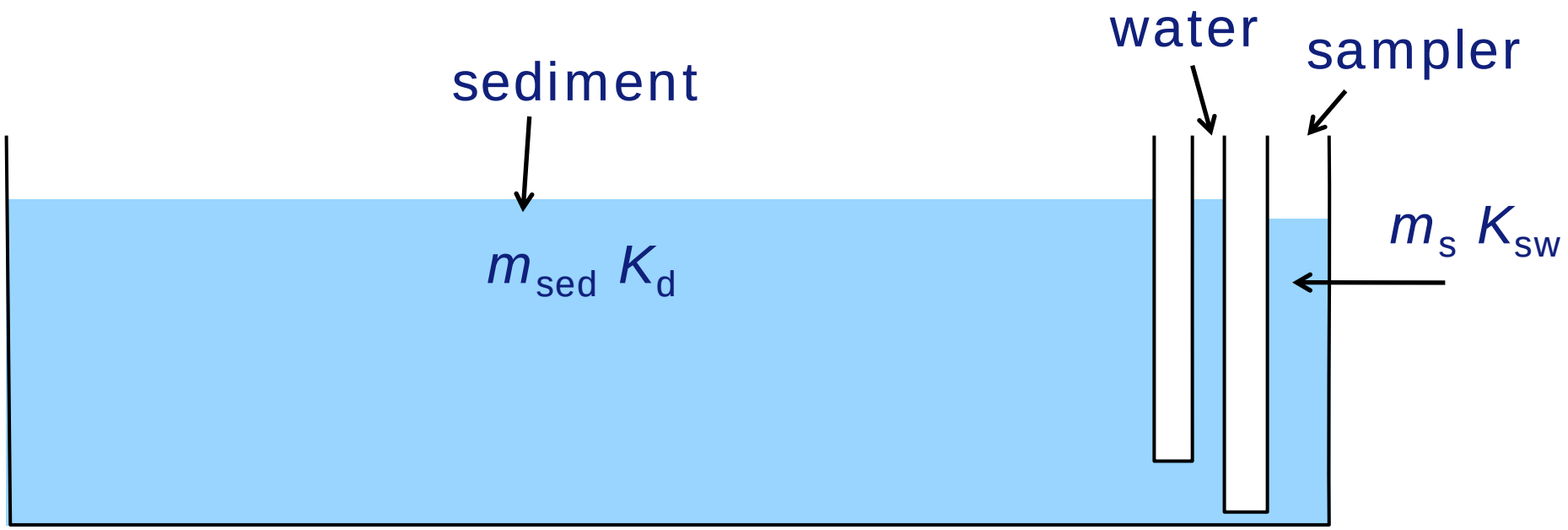
phenanthrene in 10 L water 1 g silicone

$m_s\ K_{sw}$ = 13 L

faster equilibrium

- at a lower level
- because of depletion

Sampling in sediment slurries



Pore water sniffing: $m_{sed}\ K_d + V_w >> m_s\ K_{sw}$

$C_w\ (t) \cong C_{w,0}$

Example 1: pore water sniffing

PAHs/PCBs/HCB in harbor sediments

ES&T 37: 4213-4220,2003

LDPE strips in sediment slurries and stagnant sediments

~160 g sediment (1-4% oc)

~120 mL water

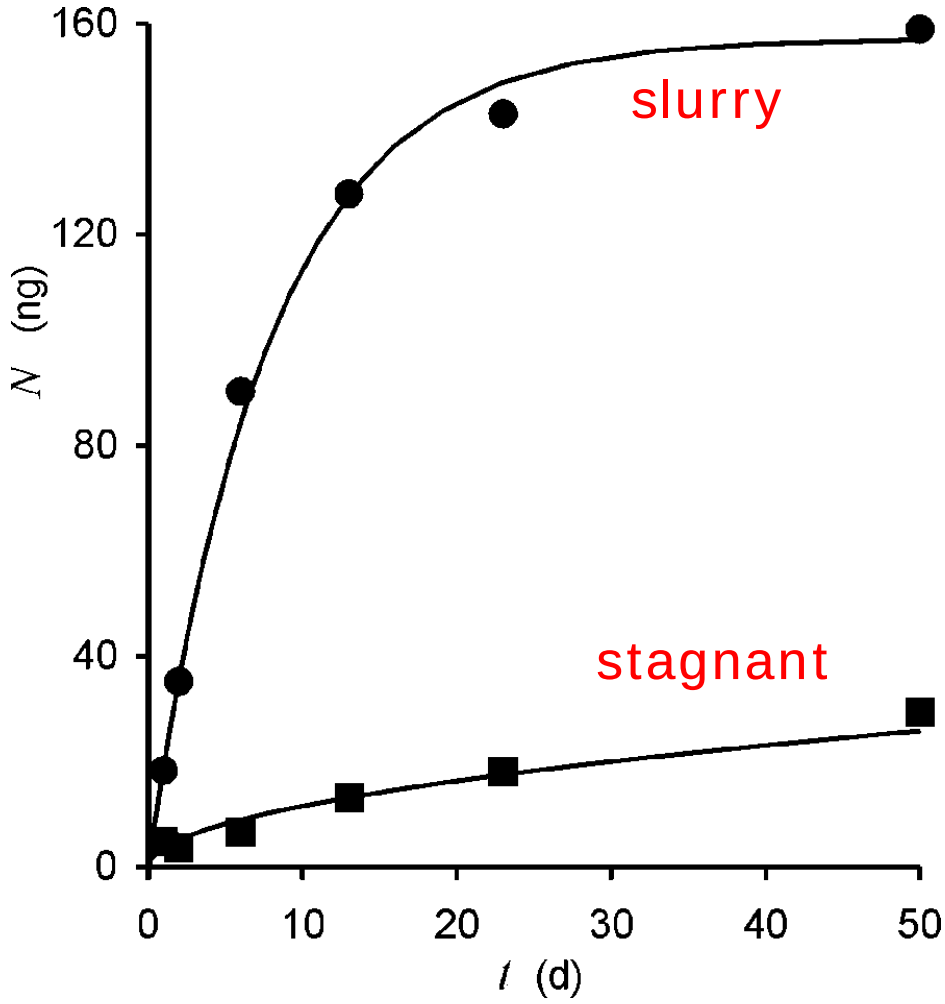
0.5 g LDPE (30x2.5 cm)

50 d exposure

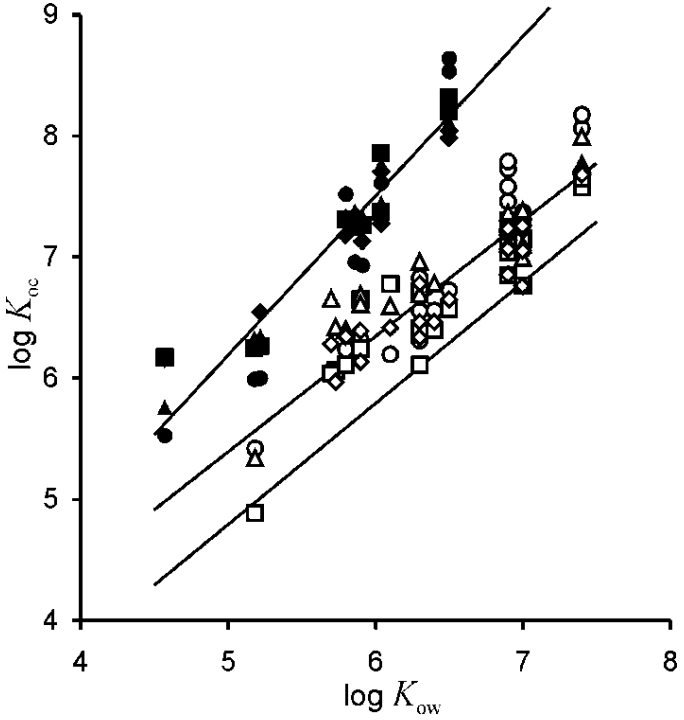
chrysene

$m_{sed}\ K_d$ ≈1000 L

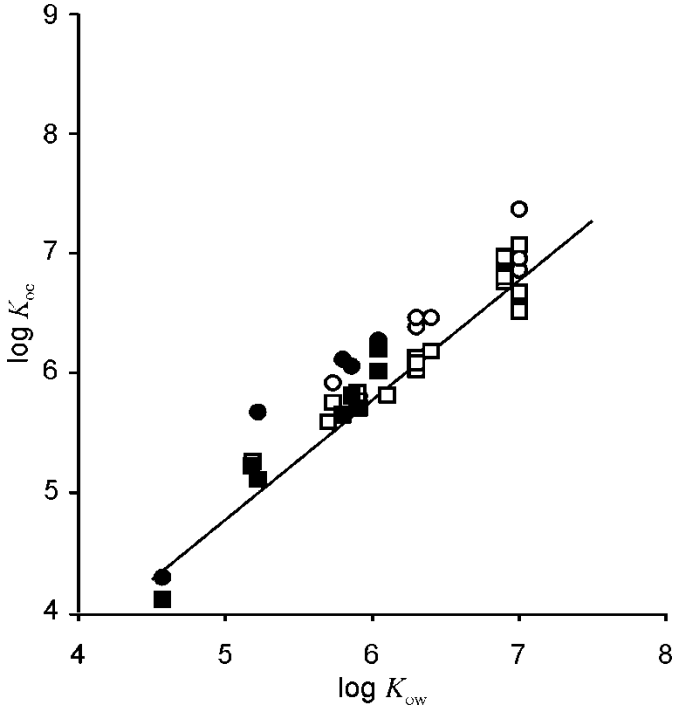
m_s K_{sw} ≈ 300 L (😐 or ☹)



K_{oc}



from C_{sed}/C_w



from uptake rates
in stagnant sediments

$$N \sim A\, C_w \sqrt{K_d}\, \sqrt{t}$$

Example 2: nondepletive and depletive extraction

PAHs/PCBs/HCB in estuarine sediments

Smedes, unpublished results

Scaling the experiment

~20 g sediment (2.5% oc)

~200 mL water

0.2, 2, 20 g silicone sheet

48d exposure

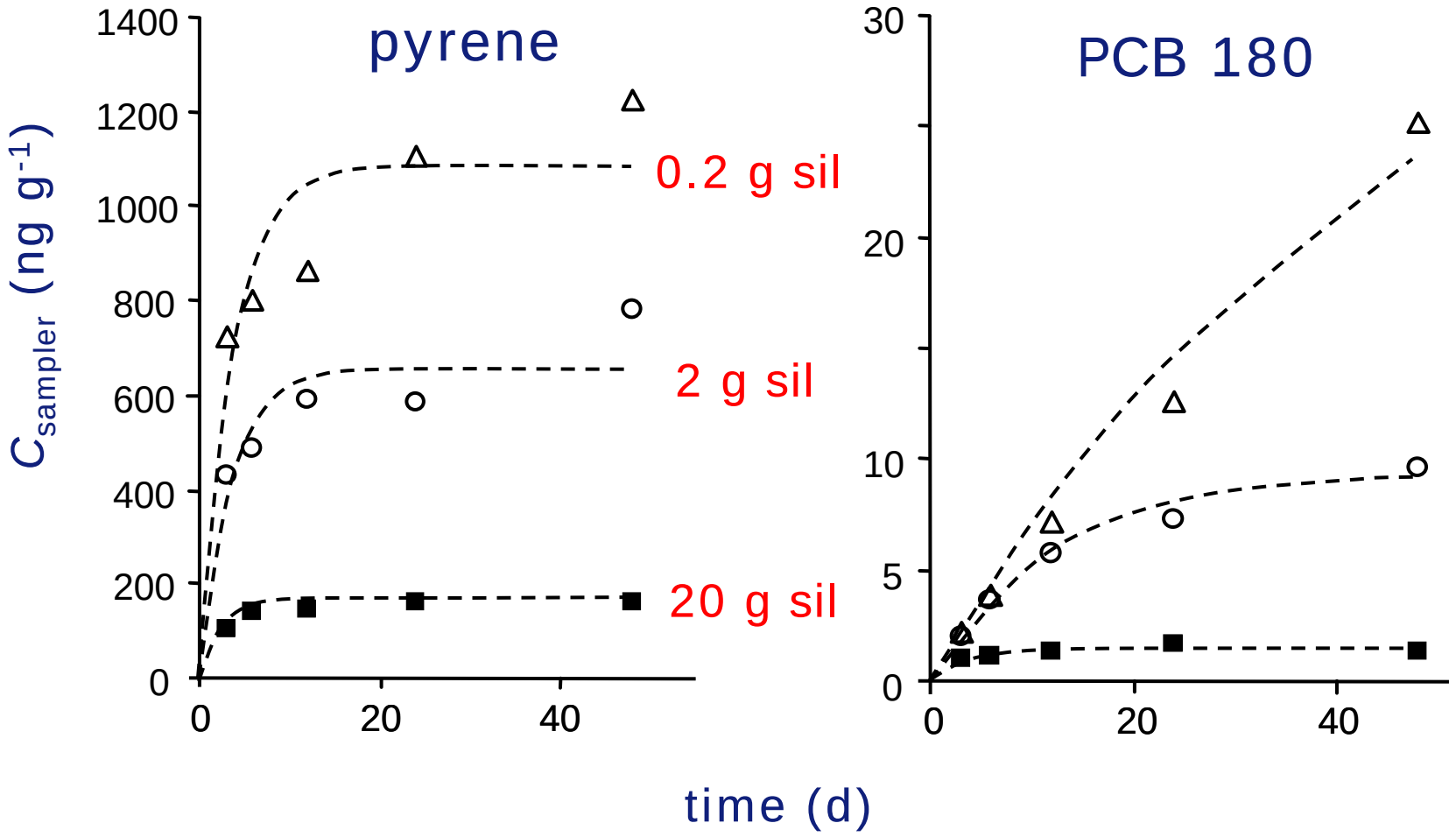
$m_{sed}\ K_d \approx 120$ L

$m_s\ K_{sw} \approx 10, 100, 1000$ L (☺)

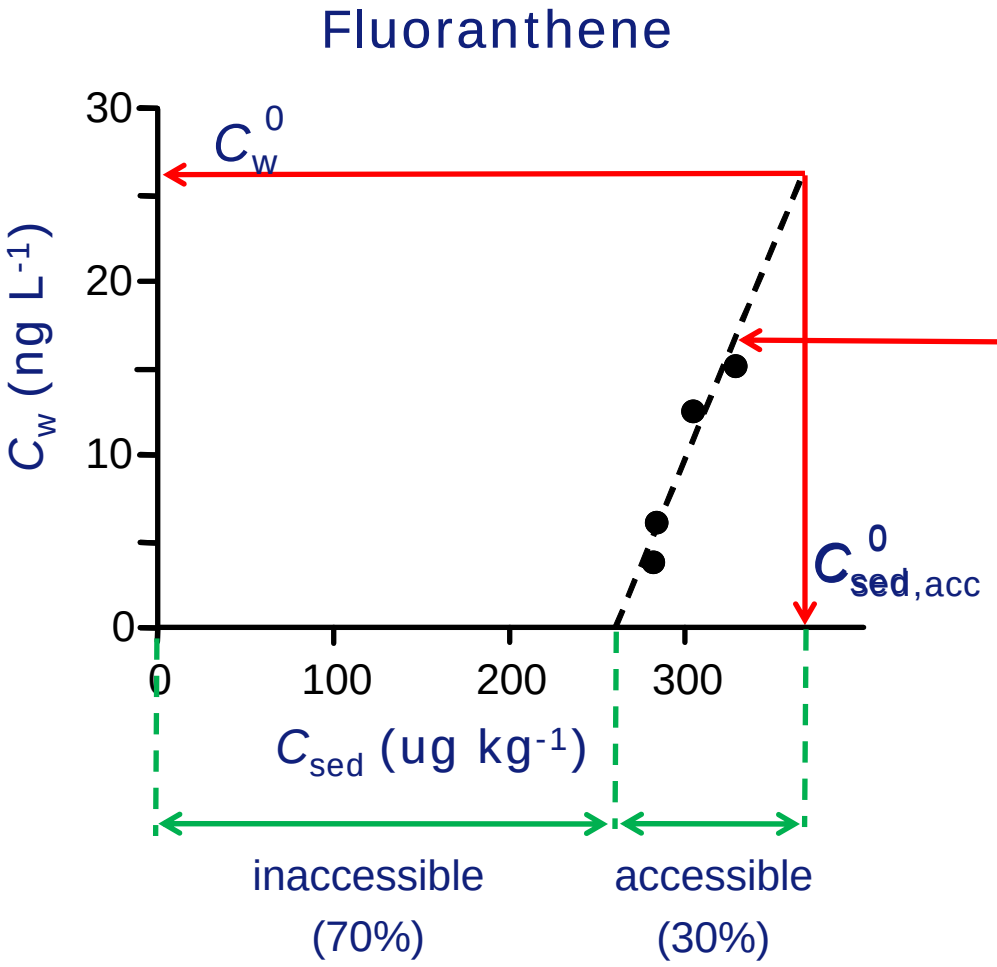
sniffing depleting

High sampler mass ⇒ depletion

20 g dw sediment, f_{oc}=0.025



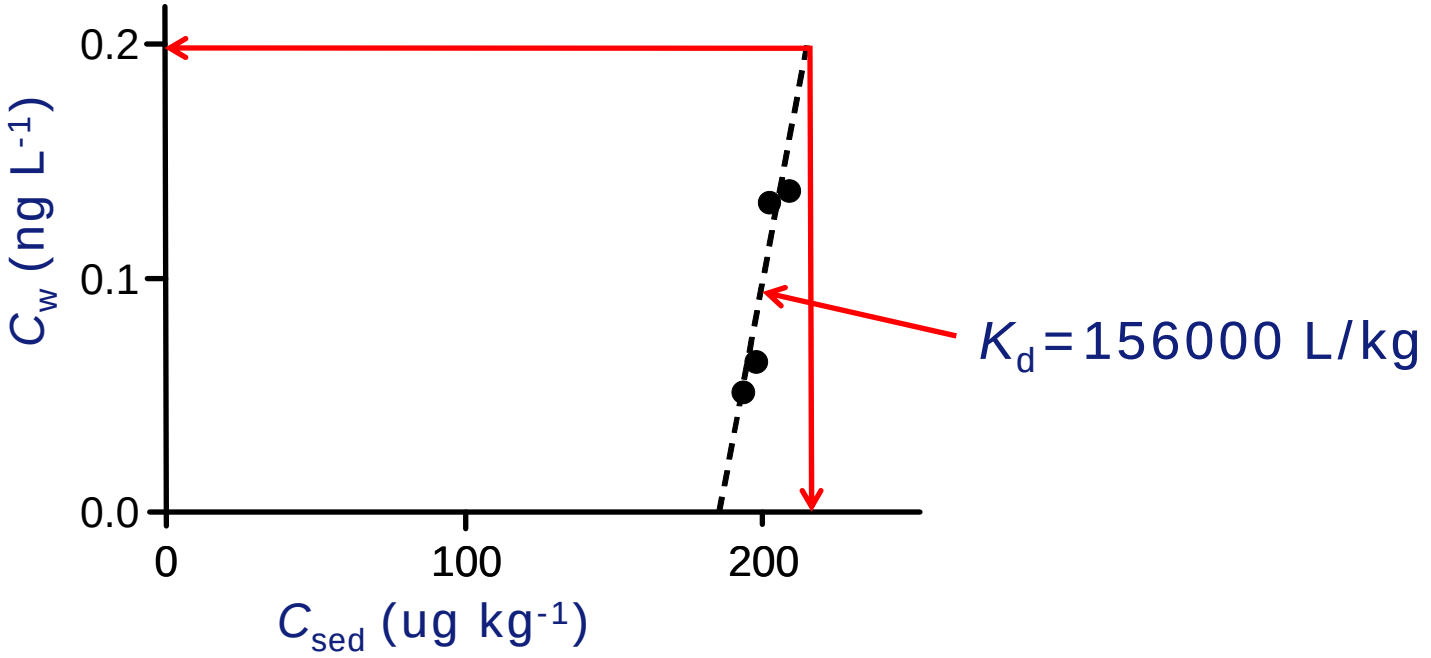
Equilibrate samplers
more mass ⇒ lower C_w⇒lower C_{sed}



$$K_d = \frac{110\ 000\ ng/kg}{27\ ng/L}$$

$$= 4100\ L/kg$$

Indeno[1,2,3-*cd*]pyrene



accessible : 14%

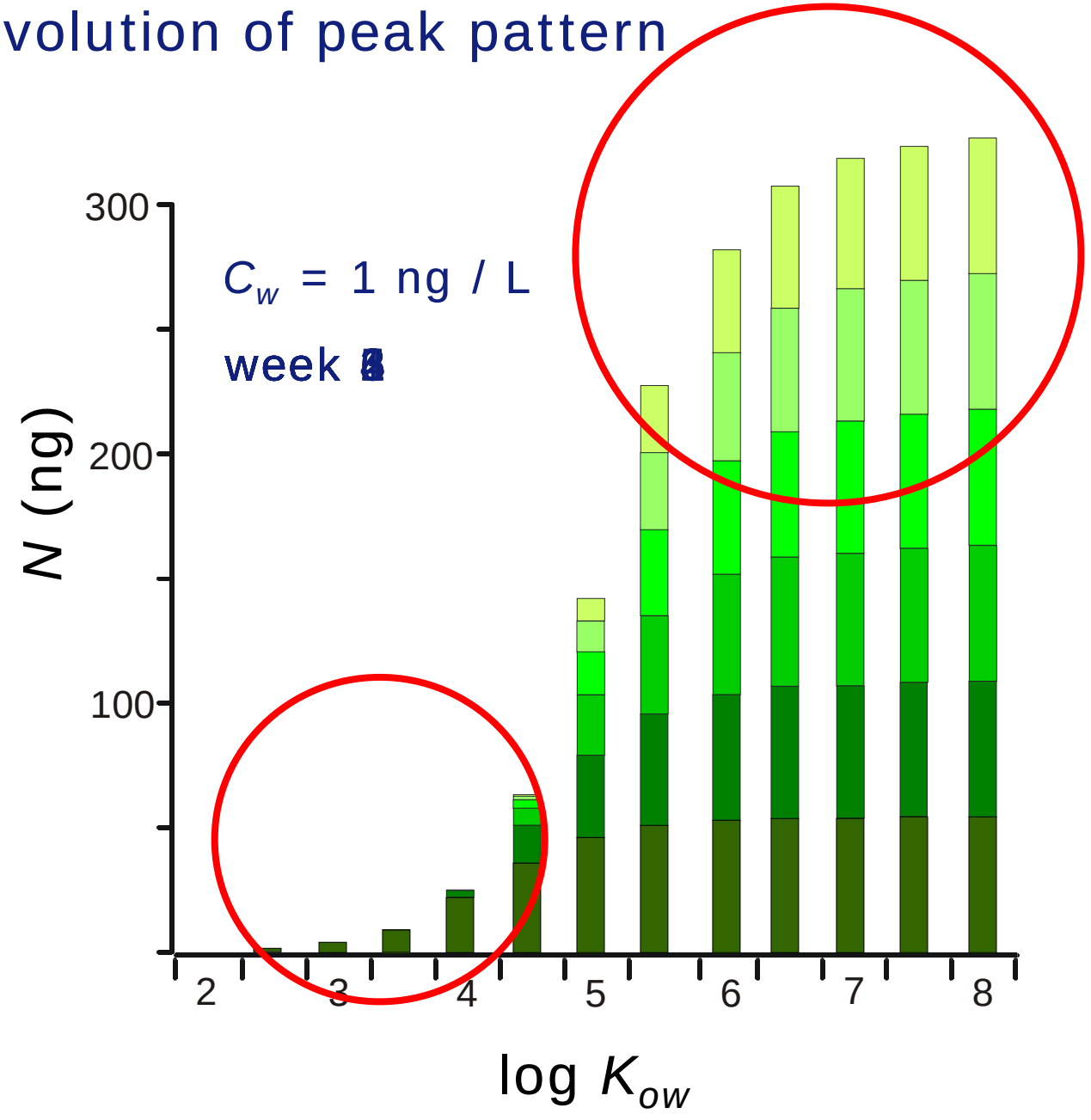
inaccessible : 86%

PSDs for sediment quality assessment: achievements & caveats

Achievements

- use R_s and $m_s K_{sw}$ to link PS to batch sampling
- non-depletive $\rightarrow C_w$
  (need R_s calibration)
- depletive $\rightarrow$ accessible fraction
  (demonstrate equilibrium)
- scaling rules are straightforward (m_{sed} & $m_{sampler}$)

Caveats

- availability of reliable K_{sw} values
- among-manufacturer variability of polymer properties
- limited PSD intercomparison

Evolution of peak pattern